

A collaboration between
ANDERSON SERANGOON JUNIOR COLLEGE
NANYANG JUNIOR COLLEGE
St. ANDREW'S JUNIOR COLLEGE

JC 2 PRELIMINARY EXAMINATION
Higher 3

CANDIDATE
NAME

CLASS

CHEMISTRY

Paper 1

9813/01

21 September 2023

2 hours 30 minutes

Candidates answer on the Question Paper.

Additional Materials: Data Booklet
 Insert

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer all questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A

Answer **all** questions.

Section B

Answer **two** questions.

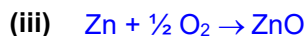
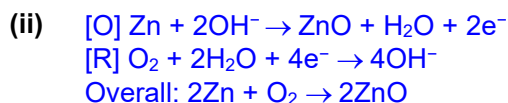
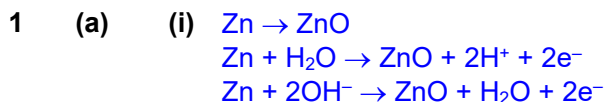
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **42** printed pages and **0** blank page and **1** insert.

Section A

Answer all questions in this section.



$$E^\circ_{\text{cell}} = +0.40 - (-1.25)$$

$$= +1.65 \text{ V}$$

$$\Delta G^\circ = -2 \times 96500 \times 1.65$$

$$= -318450 \text{ J mol}^{-1}$$

$$= -318 \text{ kJ mol}^{-1} \text{ (3 sig fig)}$$

(iv) Since air is a mixture, the pressure of oxygen in the atmosphere is less than 1 bar. This will cause the $E^\circ(\text{O}_2/\text{OH}^-)$ to be less positive resulting in a less positive E°_{cell} and hence a smaller magnitude in the Gibbs free energy change.



This will decrease the concentration of OH^- in the electrolyte and makes the $E^\circ(\text{ZnO}/\text{Zn})$ more positive which will make the E°_{cell} less positive.

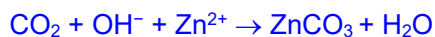
Explanation (not required in answer)



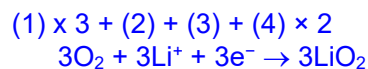
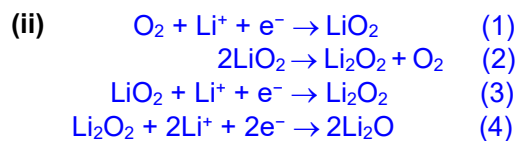
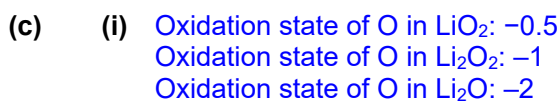
When $[\text{OH}^-]$ decreases, position of the equilibrium will shift to the right and favor the reduction reaction. This will cause $E^\circ(\text{ZnO}/\text{Zn})$ to become more positive.

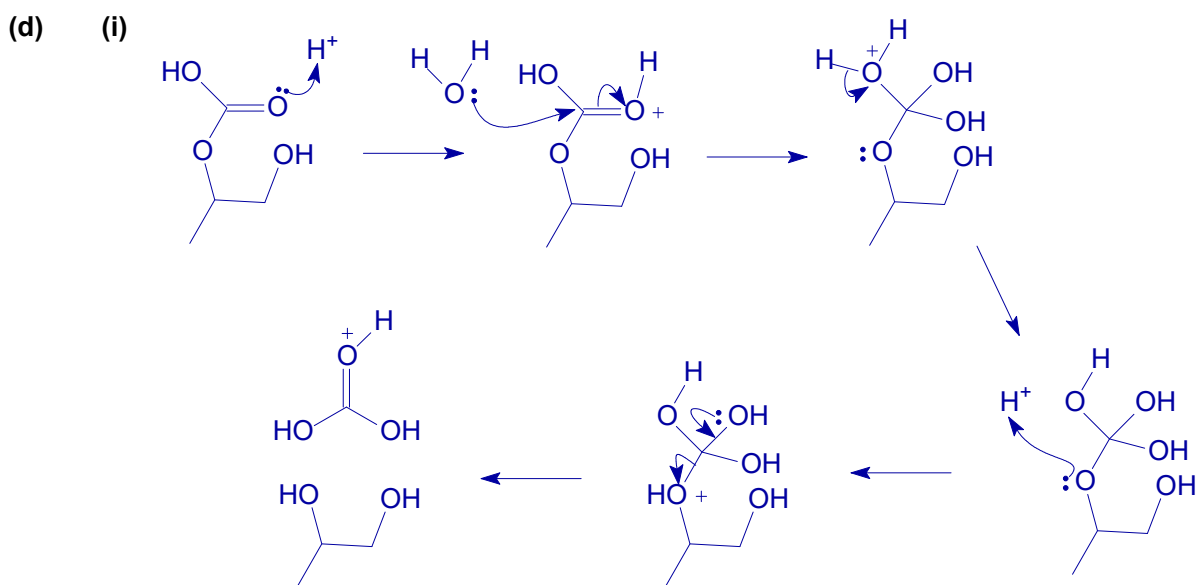
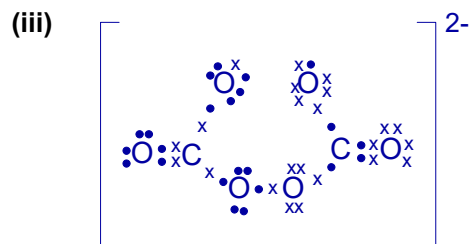
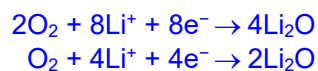
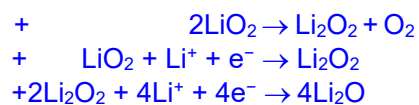
Since $E^\circ_{\text{cell}} = E^\circ(\text{O}_2/\text{OH}^-) - E^\circ(\text{ZnO}/\text{Zn})$, a more positive $E^\circ(\text{ZnO}/\text{Zn})$ will cause the E°_{cell} to become less positive.

OR

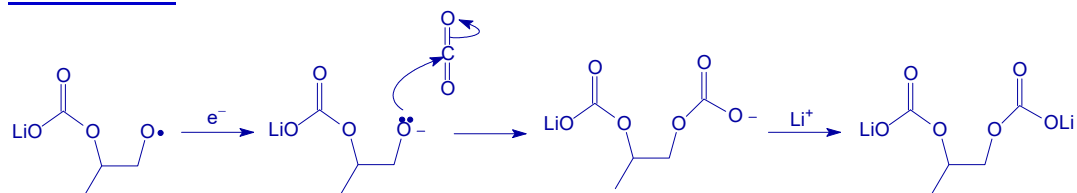


The insoluble zinc carbonate formed can clog up the pores of the carbon electrode and can prevent the reduction of oxygen to hydroxide ions.

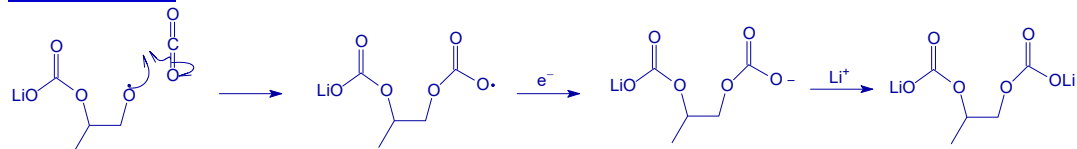




(ii) Mechanism A



Mechanism B



$$= 3.426 \times 10^8$$

$$= 3.43 \times 10^8 \text{ J}$$

$$\begin{aligned} \text{Energy produced by 1 kg of Na in a Na-air cell} &= 6328 \times 2.33 \times 3.6 \times 1000 \\ &= 5.308 \times 10^7 \\ &= 5.31 \times 10^7 \text{ J} \end{aligned}$$

(ii) Mass of Li required to produce 140 MJ of energy = $\frac{140 \times 10^6}{3.426 \times 10^8} \times 1 = 0.4086 \text{ kg}$

$$\text{Cost of Li-air cell to produce 140 MJ energy} = 0.4086 \times \$68 = \mathbf{\$27.80}$$

$$\text{Mass of Na required to produce 140 MJ of energy} = \frac{140 \times 10^6}{5.308 \times 10^7} \times 1 = 2.638 \text{ kg}$$

$$\text{Cost of Na-air cell to produce 140 MJ energy} = 2.638 \times \$2 = \mathbf{\$5.28}$$

Cost of Na-air cell to produce 140 MJ of energy is less than the cost of Li-air cell to produce 140 MJ energy. (shown)

- (iii)
- For a given mass, a Li-air cell can store more energy.
 - Since lithium has a lower atomic mass than sodium, a Li-air cell is lighter which improves the portability of the system.
 - Since Li is less reactive than Na, it is safer to store and transport.

(f) Advantage:

- Air (oxygen) is readily available.
- Metal-air cell has high energy density.

Disadvantage:

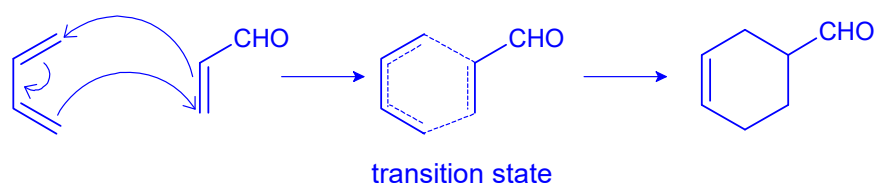
Metal-air cell with aqueous electrolyte

- There is additional cost incurred to remove carbon dioxide from air due to the use of selective membrane.
- Carbon electrode could be oxidized and will need to be replaced.
- Catalyst will be corroded over time and will need to be replaced.

Metal-air cell with organic electrolyte

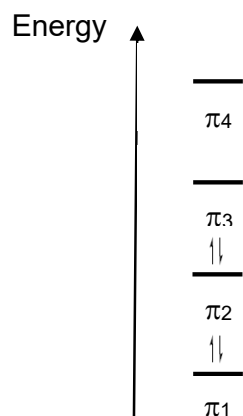
- Organic solvent is costly.
- Organic solvent is combustible.
- It produces CO₂ which is a greenhouse gas.

2 (a) (i)



- (ii) The transition state has an aromatic character due to the six delocalised π electrons. This will stabilise the transition state and lowers its energy level. Hence, the activation energy of the reaction is low enough for reaction to proceed without a catalyst.
- (iii) The cis conformation of the diene have the p orbitals of the 2 terminal carbons closer to each other such that they are able to overlap with the p orbitals of the dienophile.

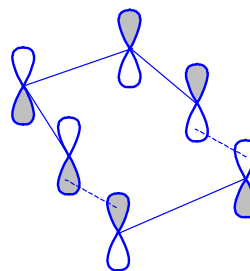
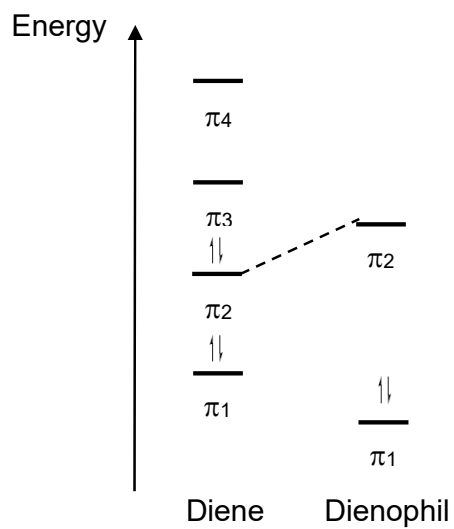
(iv)



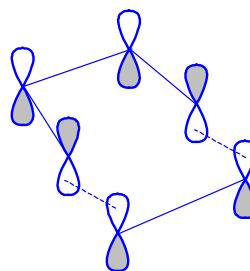
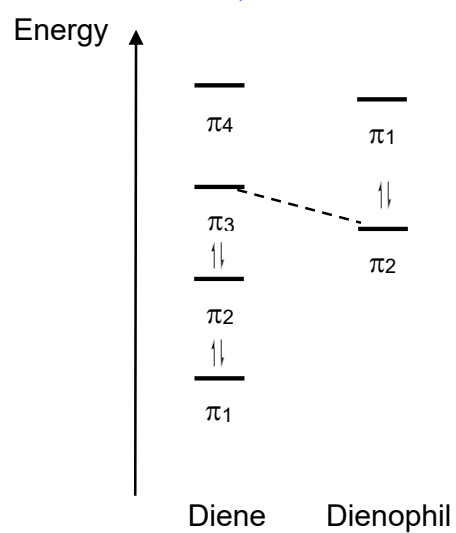
- (v) The energy level of the molecular orbitals of the dienophile for the normal demand reaction will be lower than that of the inverse demand reaction.

The electron-withdrawing group on the dienophile will be able to stabilise it (lower energy MO) through resonance effect where the π electrons are delocalised into the electron-withdrawing group. or inductive effect of electron-withdrawing group that helps to disperse the electron density of the C=C bond.

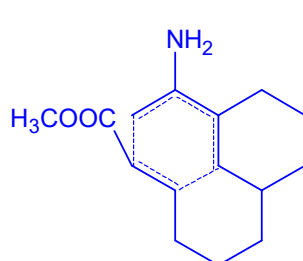
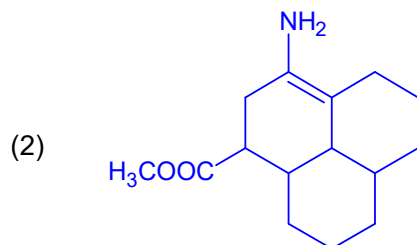
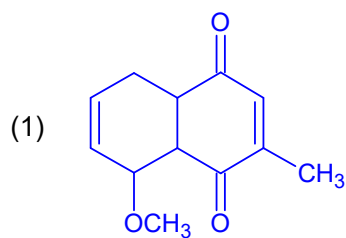
(vi) For normal demand,



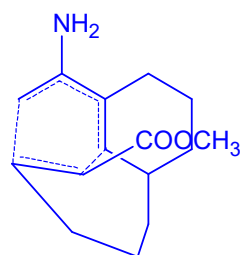
For inverse demand,



(vii)

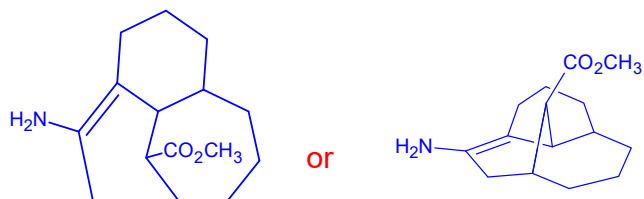


more stable transition state



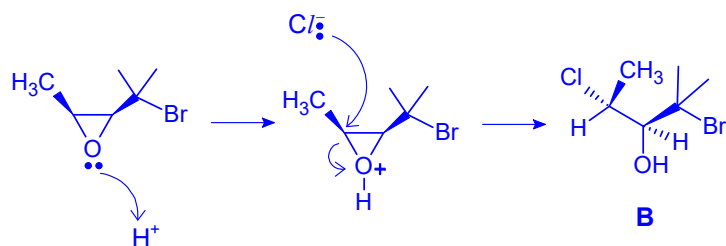
less stable transition state

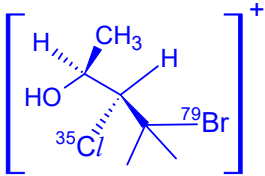
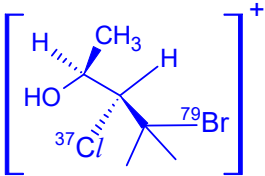
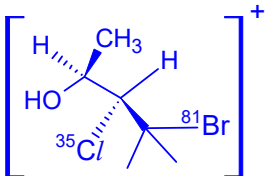
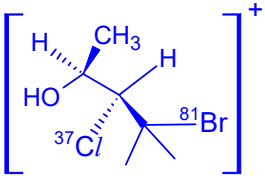
Note: Although the formation of this product did not follow the correct orientation as provided in the question (i.e. R_1 and R_2 to be in 1,4-position), it is formed via a more stable transition state. Marks will still be awarded for students who gave the 1,4-position product below.



- (b) (i) **B** is the major product as the nucleophile, Cl^- , will attack at the back side of the less hindered carbon via the $\text{S}_{\text{N}}2$ mechanism.

Nucleophilic Substitution ($\text{S}_{\text{N}}2$)



(ii) Peaks Ions	214	216	218
		 and 	
Probability	$2 \times \frac{3}{4} \times \frac{1}{2} = \frac{3}{4}$	$(2 \times \frac{3}{4} \times \frac{1}{2}) + (2 \times \frac{1}{4} \times \frac{1}{2}) = 1$	$2 \times \frac{1}{4} \times \frac{1}{2} = \frac{1}{4}$
Relative intensity	3	4	1

(iii) Mass spectrum of **B**:

- Presence of peaks at m/z 63 and 65 due to CH_3CHCl^+ and m/z 151 and 153 due to $(\text{CH}_3)_2\text{CBrCH}(\text{OH})^+$ which are absent in the mass spectrum of **C**.

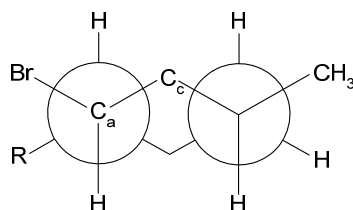
P

Mass spectrum of **C**:

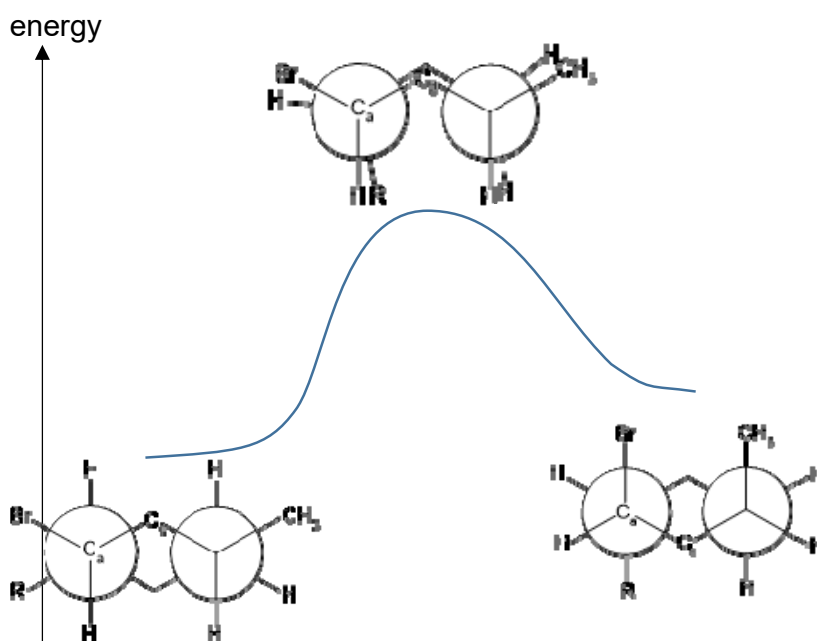
- Presence of peaks at m/z 45 due to $\text{CH}_3\text{CH}(\text{OH})^+$ and m/z 169, 171, and 173 due to $(\text{CH}_3)_2\text{CBrCHCl}^+$ which are absent in the mass spectrum of **B**.

- 3 (a) (i) When a high concentration of base is used, C_a would react with the base in the slow step, hence the rate equation would be $\text{Rate} = k_2[A][\text{base}]$.
 Note: $C_a(2^\circ \text{ halide})$ is LESS reactive with base due to steric hindrance, hence it would be the slow step in the reaction.
- (ii) For overall 1st order reaction, C_b would have to undergo either E1 or SN1 reactions, both of which are not favorable as it is a primary alkyl halide and cannot form a stable carbocation.
- (iii) $\text{Rate} = k_1[A] = k_2[A][\text{CH}_3\text{O}^-\text{Na}^+]$
 $[\text{CH}_3\text{O}^-\text{Na}^+] = \frac{k_1}{k_2} = \frac{2.07 \times 10^{-7}}{7.29 \times 10^{-8}} = 2.84 \times 10^{-3} \text{ mol dm}^{-3}$
- (b) (i) For the reaction around C_b , there is little steric hindrance around C_b , hence the nucleophile can easily approach the carbon center in a backside attack and thus result in substitution.
- (ii) Strength of base – sodium methoxide dissociates to give the methoxide ion, which is a strong base that can abstract a proton from the carbon adjacent to C_a , resulting in elimination.
 Size of base – However, because the methoxide ion is small, it can also attack the central carbon C_a in a substitution reaction.

(iii)



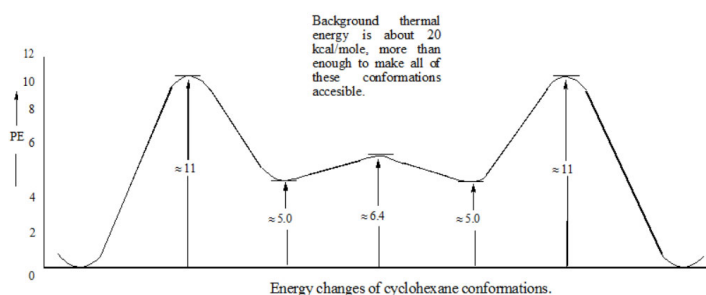
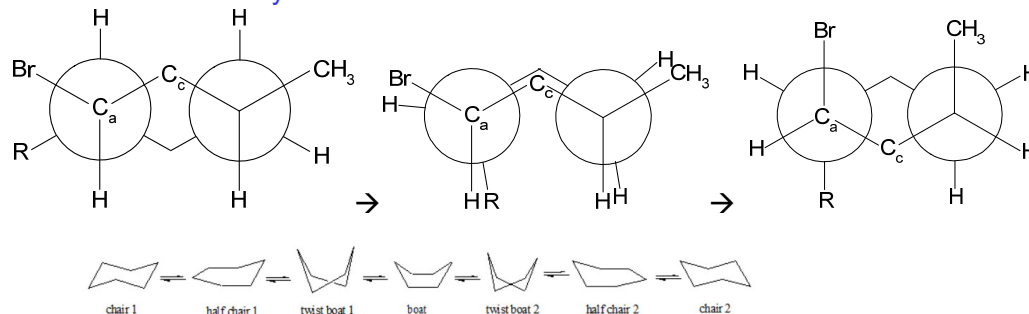
(iv)



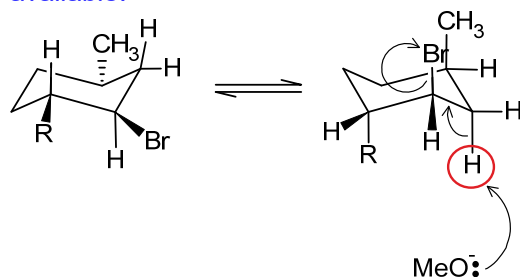
The most stable conformation with the lowest energy of the compound is when the bulky substituent groups are in the equatorial positions. When it shifts to a boat conformation, the eclipsed conformation results in an unstable conformation with high energy.

When it shifts to the other chair conformation, the gauche conformation of the substituent groups results in 1,3 diaxial repulsion and hence higher energy compared to the other chair conformation.

Note: The actual shift from chair to boat conformation is actually even more complex, but this is not in the syllabus.

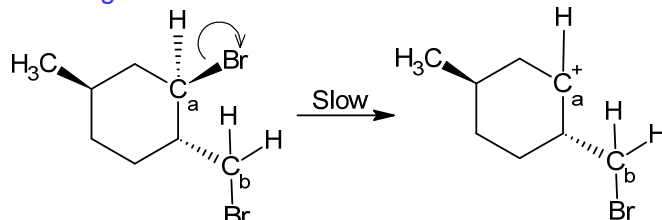


- (v) In order for E2 to occur, A has to invert its conformation [1] so that the Br atom is anti-periplanar with a hydrogen atom so that it can undergo trans elimination. However, after inverting the conformation, there is only one anti-periplanar hydrogen available.

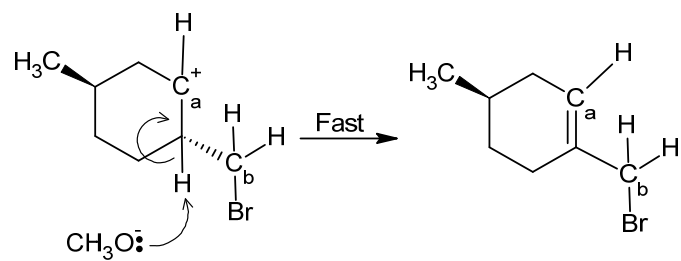


Hence **F** is not formed.

- (c) (i) Total percentage of B+C+F > Total percentage of D+E
E1 was favored over S_N1 .
- (ii) C_a can undergo either E1 or S_N1 reaction. The first step of the mechanism involves breaking the C-Br bond to form the carbocation.



However, since the methoxide ion is a strong base, it can abstract a proton from an adjacent carbon than attack the carbocation intermediate, resulting in an elimination reaction rather than a substitution.



G is the Zaitsev product as it is the more substituted product.

- (iii) The use of a bulky base increases the steric repulsion between the base and the compound, increasing the activation energy.

The base would react preferentially with the less hindered proton, forming the less substituted product.

Note: Step 2 is possible as S_N1 mechanism can occur with primary allylic halides that are capable of forming extremely stable carbocations, particularly in very polar solvents.

Section B

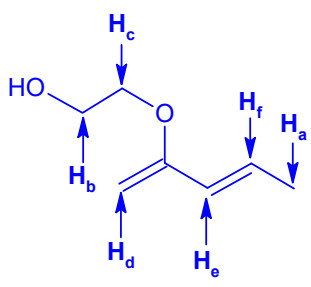
Answer **two** questions in this section.

- 4 (a) (i) $\text{rate} = k[\text{P}]$
 Since the question mentioned that it is a multi-step reaction, the reaction is $\text{S}_{\text{N}}1/\text{E}1$.
- (ii)
 - R configuration.
 - The leaving Cl^- is being attracted to the carbocation even after cleavage, which prevent complete solvation and separation. The Cl^- and carbocation recombines to give the original reactant is also known as *internal return (or ion-pair interaction)*.
 - As a result, this causes steric hindrance on one face by the departing Cl^- , favouring back-side attack by the OH^- .
- (b) (i) Since compounds **Q** and **S** are positional isomers, number of carbon in compound **S** = 7
- $$n = \frac{100}{1.1} \times \frac{A_{\text{M+1}}}{A_{\text{M}}}$$
- $$7 = \frac{100}{1.1} \times \frac{1}{x}$$
- $$x = 12.99 = 13.0$$
- (ii)
 - Infra-red spectrum of compound **S**, 3620 cm^{-1} and 3640 cm^{-1} : presence of 2 OH groups
 Infra-red spectrum of compound **T**, 3630 cm^{-1} : presence of 1 OH group
 - m/z value of 31 belongs to $[\text{CH}_2\text{OH}]^+$ fragment and m/z value 45 belongs to $[\text{CH}_2\text{CH}_2\text{OH}]^+$.
 - δ 2.39 ppm and δ 4.22 ppm of Fig. 4.2 (compound **S**), and δ 3.00 ppm of Fig. 4.3 (compound **T**) belong to labile protons from OH groups, which disappear upon addition of D_2O as they undergo proton exchange with the solvent.

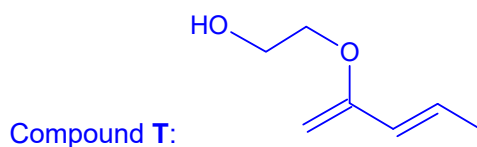
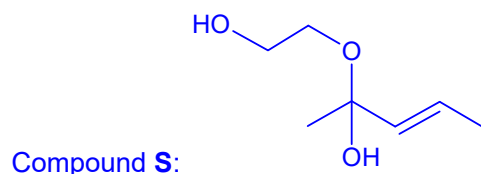
Compound S			
δ / ppm	integration	multiplicity	Explanation
1.46	3	singlet	Three protons (H_{a}) belong to CH_3 group that is bonded to a tertiary carbon. It is a singlet and suggest that there are no protons on the adjacent carbon.
1.73	3	doublet	Three protons (H_{b}) belong to CH_3 group that is bonded to CH . It is a 1:1 doublet and suggest that there is one proton (H_{f}) on the adjacent carbon.
3.52	2	triplet	Two protons (H_{c}) belong to CH_2 group that is bonded to CH_2 , next to electronegative oxygen atom. It is a 1:2:1 triplet and suggest that there are two protons (H_{d}) on the adjacent carbon.
3.86	2	triplet	Two protons (H_{d}) belong to CH_2 group that is

			bonded to CH ₂ , next to electronegative oxygen atom. It is a 1:2:1 triplet and suggest that there are two protons (H _c) on the adjacent carbon.
5.45	1	doublet	One protons (H _e) belong to alkene CH group that is bonded to a CH group. It is a 1:1 doublet and suggest that there is one proton (H _f) on the adjacent carbon.
5.57	1	multiplet	One protons (H _f) belong to alkene CH group that is bonded to a CH and CH ₃ groups. It is a multiplet and suggest that there is one proton (H _e) and three proton (H _a) on the adjacent carbon.

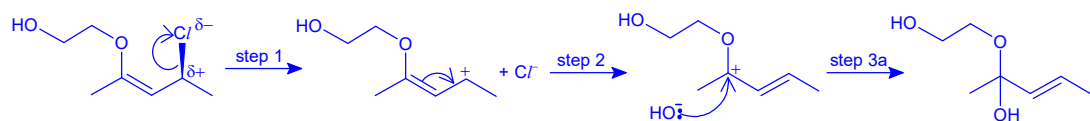
Note: assigning of δ 3.52 ppm and δ 3.86 ppm are interchangeable

Compound T 			
δ / ppm	integrati on	multiplic ity	Explanation
1.64	3	doublet	Three protons (H _a) belong to CH ₃ group that is bonded to an alkene CH group. It is a doublet and suggest that there is one proton (H _f) on the adjacent carbon.
3.58	2	triplet	Two protons (H _b) belong to CH ₂ group that is bonded to CH ₂ , next to electronegative oxygen atom. It is a 1:2:1 triplet and suggest that there are two protons (H _c) on the adjacent carbon.
4.09	2	triplet	Two protons (H _c) belong to CH ₂ group that is bonded to CH ₂ , next to electronegative oxygen atom. It is a 1:2:1 triplet and suggest that there are two protons (H _d) on the adjacent carbon.
5.09	2	singlet	Two protons (H _d) belong to CH ₂ group that is bonded to the alkene carbon with no protons. It is a singlet and suggest that there is no protons on the adjacent carbon.
5.93	1	doublet	One protons (H _e) belong to alkene CH group that is bonded to a CH group. It is a 1:1 doublet and suggest that there is one proton (H _f) on the adjacent carbon.
6.08	1	multiplet	One protons (H _f) belong to alkene CH group that is bonded to a CH and CH ₃ groups. It is a multiplet and suggest that there is one proton (H _e) and three proton (H _a) on the adjacent carbon.

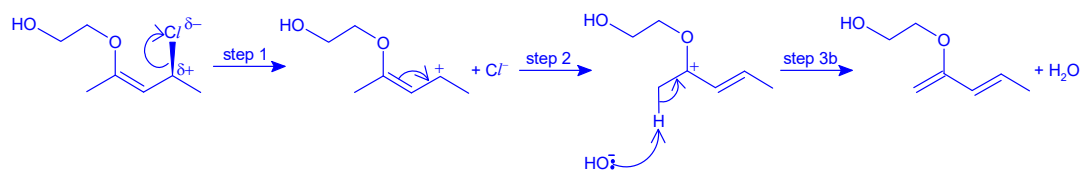
Note: assigning of δ 3.58 ppm and δ 4.09 ppm are interchangeable



(iii) Nucleophilic Substitution (S_N1)



Elimination ($E1$)



(iv) •

orbital of carbocation overlap with π electron cloud of $C=C$ double bond, π electrons delocalise and disperse the positive charge.

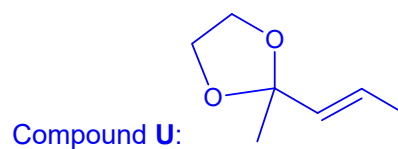
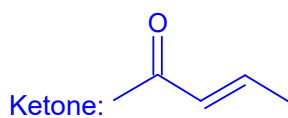
•

orbital of oxygen overlap with p orbital of carbocation, lone pair of electrons delocalise and further disperse the positive charge.

•

•

(c)



- 5 (a) (i) Simple molecules absorb the frequency of IR radiation that matches to the stretching or bending vibrational frequency of the bond.

The absorption of IR radiation will only take place if the vibration causes a change in dipole moment of the molecule.

- (ii) Both CO_2 and CSO are linear molecules. They should both have 4 vibrational modes ($3N-5$) – symmetric stretching, asymmetric stretching and 2 bending modes.

For CO_2 , there are only 2 IR active vibrational modes (asymmetric stretching and bending mode). As both bonds in CO_2 are $\text{C}=\text{O}$, the dipole moments cancel out for symmetric stretch and are not IR active. The 2 bending modes are degenerate and hence show up as one peak rather than two.

For CSO , being similar in structure with CO_2 has the same number of vibrational modes. However, as it is made up of one $\text{C}=\text{O}$ and one $\text{C}=\text{S}$ bond, the dipole moments are not cancelled out and hence the symmetric stretching is IR active and all 4 vibrational modes are IR active.

- (iii) For paracetamol, strong and sharp peaks at $3200 - 3600 \text{ cm}^{-1}$ suggests presence of $\text{O}-\text{H}$ stretch in phenol and a weak peak at $3300 - 3500 \text{ cm}^{-1}$ suggest presence of $\text{N}-\text{H}$ stretch in amide. For aspirin, the $\text{O}-\text{H}$ stretch due to carboxylic acid will be strong and broad at a lower range of $2500 - 3000 \text{ cm}^{-1}$.

For paracetamol, there is one sharp peak at $1640 - 1690 \text{ cm}^{-1}$ due to presence of $\text{C}=\text{O}$ stretch in amide. For aspirin, there will be two peaks around the same region due to $\text{C}=\text{O}$ stretch correspond to the ester (1710 to 1750 cm^{-1}) and carboxylic acid ($1680 - 1730 \text{ cm}^{-1}$).

For aspirin, there are two strong peaks at $1050 - 1330 \text{ cm}^{-1}$ and 1210 to 1440 cm^{-1} due to presence of $\text{C}-\text{O}$ stretch in ester and in carboxylic acid. For paracetamol, there is only one peak for $\text{C}-\text{O}$ in phenol.

- (b) (i) No. of carbon atoms in $\text{X} = \frac{100 \left(\frac{15.4}{100} \right)}{1.1} = 14$

(ii)

δ / ppm	integration	multiplicity	Deduction
0.90	6	d	2 x $-\text{CH}_3$ next to a $-\text{CH}$
1.90	1	m	$-\text{CH}$ next to two $-\text{CH}_3$
2.10	2	d	$-\text{CH}_2$ next to $-\text{CH}$ and $-\text{C}=\text{O}$
4.70	2	d	$-\text{CH}_2$ next to $-\text{CH}$ and $-\text{O}$
6.40	1	m	$-\text{CH}=\text{C}$
6.60	1	d	$-\text{CH}=\text{CH}$ next to benzene ring
7.20	5	m	Benzene ring with one substitute

From NMR, no. of H atoms = 18

Therefore, number of oxygen is = $(218 - 18 \times 1 - 14 \times 12) / 16 = 2$

Molecular formula is $C_{14}H_{18}O_2$

(iii) IR:

- Strong and sharp at 1750 cm^{-1} due to $C=O$.
- Absence of alcohol as there is no signal at 3200 to 3600 cm^{-1} .

Reactions:

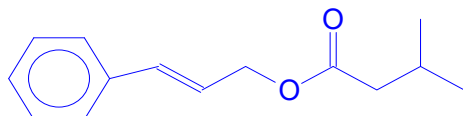
- X undergoes oxidative cleavage of alkene and acidic hydrolysis of ester upon treatment with hot acidified $KMnO_4$, loss of two carbons
- Ethandioic acid is formed after the reaction with $KMnO_4$ which forms 2 mol of CO_2 .

$$\text{Degree of unsaturation} = \frac{2 \times \text{no. of C} + 2 - \text{no. of H}}{2} = \frac{2 \times 14 + 2 - 18}{2} = 6$$

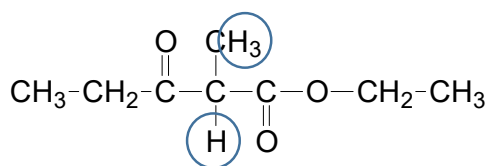
Structure in X	Degree of unsaturation
benzene	4
$C=O$ from ester	1

Hence there is only one $C=C$ that contributes a degree of unsaturation of 1 that will add up to 6 for compound X .

X :



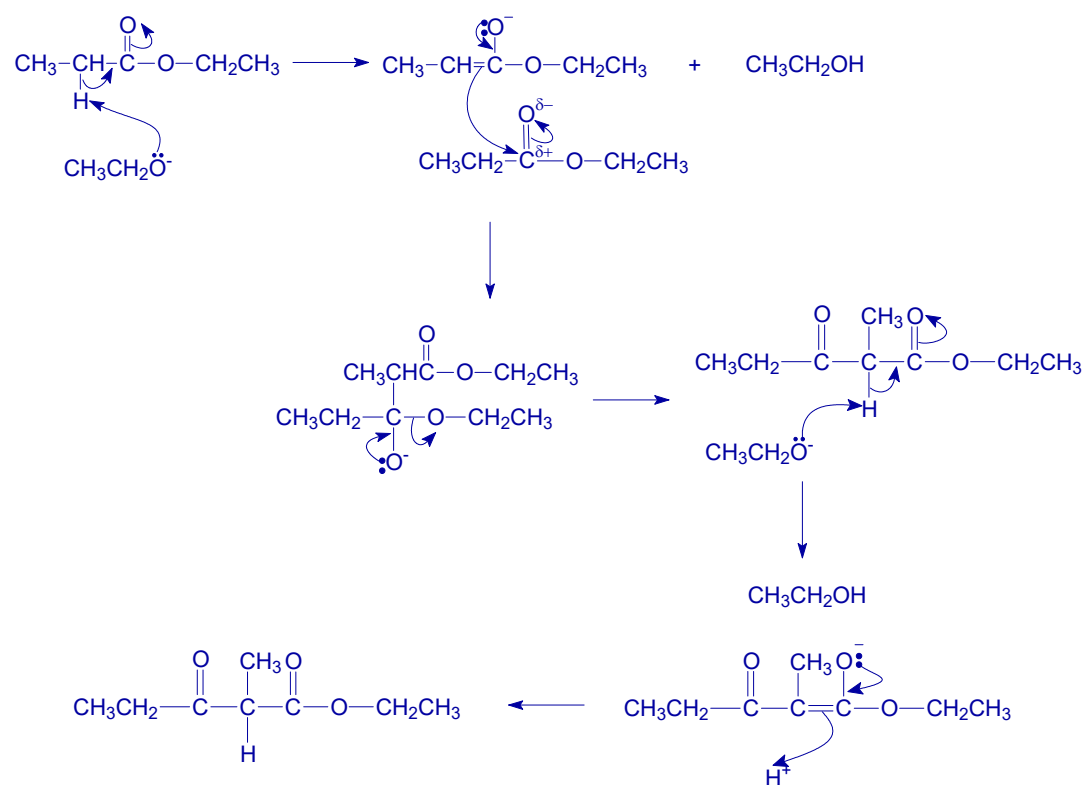
(c) (i) β -keto ester will have two additional signals:



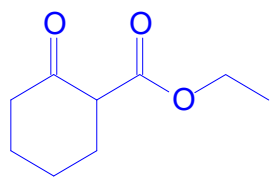
$-CH$ will have a chemical shift value of approximately 2.2 to 3.0 larger than that for the $-CH_2$ group next to $C=O$ in the ester as this proton is next to two $C=O$ groups. Its splitting pattern will be a quartet as it is next to a $-CH_3$.

$-CH_3$ will have a chemical shift of approximately 0.9 to 1.7 similar to the $-CH_3$ groups in the ester as they are both alkanes. Its splitting pattern will be a doublet as it is next to a $-CH$.

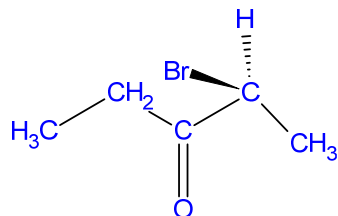
(ii)



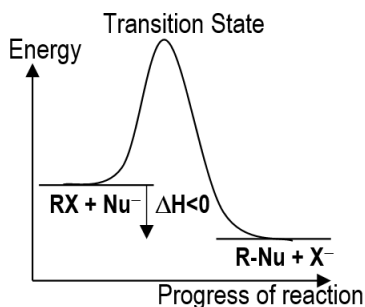
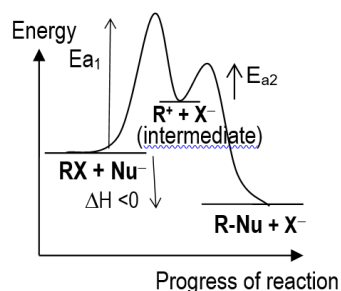
(iii)



6 (a) (i)



(ii)

Energy Profile of S_N2 reactionEnergy Profile of S_N1 reaction

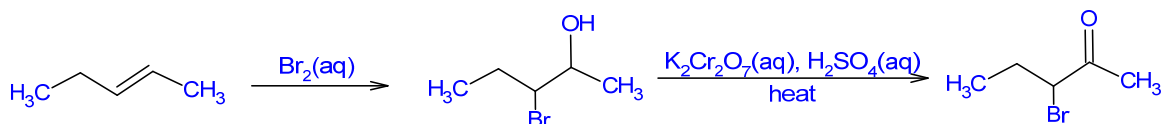
(iii) At time $t = 0$, there is 100% (*S*)-2-bromopentan-3-one which has an optical rotation value of $+30^\circ$.

When 70% of (*S*)-2-bromopentan-3-one undergoes conversion via S_N1, the resulting mixture contains

- 30% (*S*)-2-bromopentan-3-one (30% $\times$ $+30^\circ$)
- 35% (*S*)-2-cyanopentan-3-one (35% $\times$ -30°) [optional]
- 35% (*R*)-2-cyanopentan-3-one (35% $\times$ $+30^\circ$) [optional]

Giving a resulting optical rotation of $+9.0^\circ$

(b)



Allow for KMnO₄, H₂SO₄(aq), heat cannot allow for alkaline

(c)

(i) Using the equation $E_a = A + B\Delta H$,

For the production of 2-chlorobutane: $+21.5 = A + B(-62.9)$ -----(1)

For the production of 2-bromobutane: $+23.0 = A + B(-72.8)$ -----(2)

Taking (1) – (2): $-1.5 = B(9.9)$

$$B = -0.1515$$

Hence, $+21.5 = A - 0.1515(-62.9)$

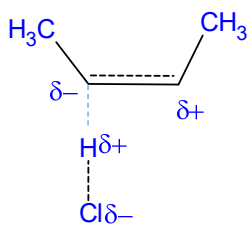
$$A = 11.97$$

For the enthalpy change of reaction for production of 2-iodobutane

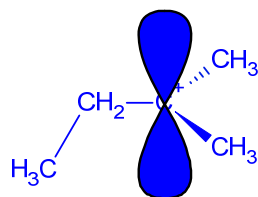
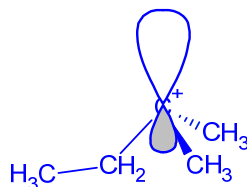
$$+24.5 = 11.97 - 0.1515\Delta H$$

$$\Delta H = -82.7 \text{ kJ mol}^{-1}$$

(ii)



(iii)

 sp^2 hybridisation sp^3 hybridisation

(iv) The structure where the carbon carrying the positive charge is sp^2 hybridised is more stable.

This is because the sp^2 orbitals of this structure, which are filled, are lower in energy level than the sp^3 orbitals of the other structure.

Also, there is less steric repulsion between the bulky methyl groups in this structure, since they are further apart (at 120°) to each other, as compared to the other structure (109° apart).

(d)

(i) Any 2 of the following is accepted

- The chlorine atom would form a partial double bond via its p orbitals with the sp^2 C atom, which is significantly stronger than (sp^3) C-Cl bond
- The carbon being attacked is electron rich (part of the alkene function group) and hence would not be susceptible to attack from the electron rich hydroxide ion
- The OH^- ion would have to attack the carbon in the plane of the carbon-carbon double bond (facing steric hindrance from the $=CH_2$ group)

(ii) The secondary carbocation formed ($CH_3CH_2C^+H/CH_3$) is significantly more stable due to the 2 electron-donating alkyl groups (and the additional electron density from the delocalisation of lone pairs of electrons from Cl) bonded to the positively charged carbon as compared to the primary carbocation ($CH_3CH_2CH_2C^+H_2$).

(iii) Purple $KMnO_4$ decolourises, (green gas, white fumes observed)

Award [2] for either of the following balanced equations :

